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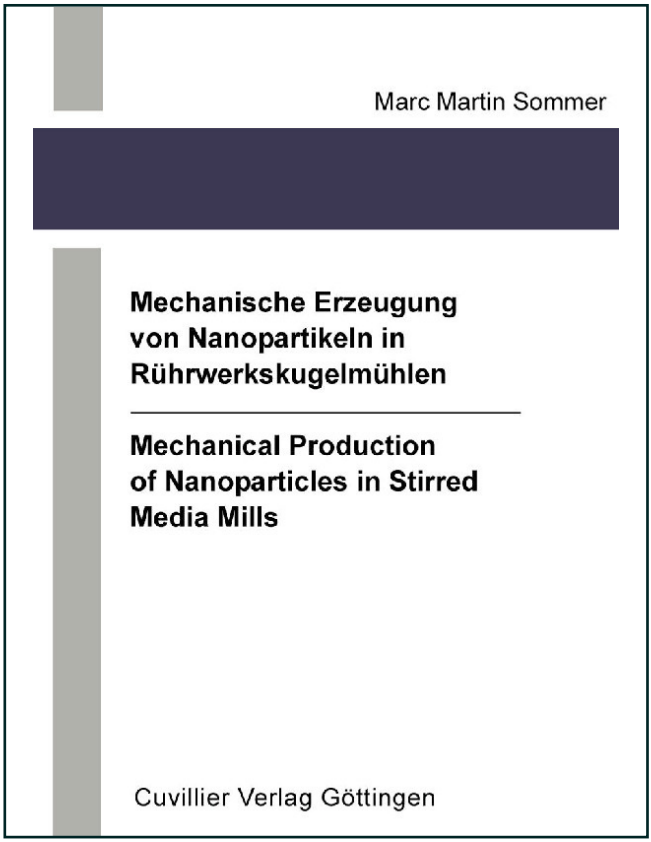
Mechanical Production of Nanoparticles in Stirred Media Mills



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CHAPTER 1

Introduction

Nanoparticles are increasingly used in many areas of the chemical and pharmaceutical industry as well as in the ceramic and microelectronic industry. Applications for sub-micron particles are for example pigments, nanocomposites, drug delivery and ceramic materials. Besides the direct synthesis of these materials by chemical methods, wet grinding in stirred media mills is a suitable method for the production of nanoparticles, since the high energy densities, which are necessary to produce nanoparticles, can be achieved in stirred media mills [**1**]. The manufacturing of fine particles in stirred media mills is influenced next to machine parameters (e.g. design, function and size of the mill) and process parameters (e.g. rotational speed, filling degree etc.) by interparticle interactions. These interactions influence the stability of the milling suspension against coagulation as well as the rheology of the suspension. Particles in the order of 1 μm and below feature a high mobility due to Brownian diffusion. This leads to a high collision frequency between the particles. If non-stabilized particles collide, agglomerates strong enough to withstand the grinding process may be formed. This effect has limited the milling process in the past. A grinding limit was postulated for particle sizes of around 0.5 μm [**3, 4**]. By producing particles smaller than a median particle size of 1 μm a steady state between breakage and agglomeration exists in the milling process. This equilibrium is controlled by interparticle interactions as well as the milling conditions. The more the particles decrease in size the more the interparticle forces between the particles become dominant. Attractive forces lead to agglomerates when the particles collide, thus acting against the comminution process. To prevent this agglomeration process the particles in the mill must be stabilized by increasing the repulsive forces in the suspension. This will move the steady state to smaller particle sizes. To study the grinding limits of particle sizes below 1 μm a detailed understanding of the agglomeration process and its mechanism is needed. This is why this work focuses on the agglomeration process and on the stability of the suspension against agglomeration. In this study primary nanoparticles of a diameter of around 30 nm are considered and the agglomeration process under perikinetic and orthokinetic conditions is observed. On basis of this the agglomeration and dispersing process is studied in a stirred media mill. It could be shown that the agglomeration of the particles is accelerated until the steady state between agglomeration and deagglomeration is reached. Furthermore, it is shown that this steady state can also be reached by real breakage from large particle sizes. This work points out that

nanomilling in stirred media mills is possible in aqueous suspensions with electrostatic stabilization if particle stability and suspension rheology are carefully controlled.

Furthermore, the study was extended to non-aqueous systems, because of the high industrial demand on nanoparticles in organic media. The state and the properties of particle surfaces in the liquid phase are discussed. Based on this, possibilities to influence the interparticle interactions and with it the stabilization of the particles are described. Milling studies with electrostatic and steric stabilization mechanisms in organic solvents were conducted and compared to the milling behavior in water.

Einleitung

Sowohl in der chemisch- pharmazeutischen Industrie als auch in der keramischen und mikroelektronischen Industrie werden immer häufiger Nanopartikel eingesetzt. Anwendungen sind zum Beispiel Pigmente, Nanokomposits, gezielte Pharmakotherapie oder keramische Materialien. Neben der direkten Synthese von diesen Materialien durch chemische Methoden, sind nass betriebene Rührwerkskugelmühlen für die Produktion von Nanopartikeln durch mechanische Zerkleinerung besonders geeignet, da sie die hohen Leistungsdichten zur Verfügung stellen, die für die Zerkleinerung in dem Nanometerbereich erforderlich sind [**1**]. Die Herstellung von feinen Partikeln in Rührwerkskugelmühlen wird neben Maschinenparametern (z.B. Geometrie, Funktionsweise und Abmessungen der Mühle) und Prozessparametern (z.B. Umfangsgeschwindigkeit, Mahlkörperfüllgrad usw.) von interpartikulären Wechselwirkungen beeinflusst. Diese Wechselwirkungen beeinflussen sowohl die Stabilität der Mahlgutsuspension gegen Koagulation als auch die Rheologie der Suspension. Partikel in der Größenordnung von 1 μm und kleiner besitzen aufgrund der Brownschen Diffusion eine hohe Beweglichkeit. Dies führt zu einer hohen Kollisionsrate zwischen den Partikeln. Wenn nicht stabilisierte Partikel zusammenstoßen, können Agglomerate entstehen, die größer als die Ausgangspartikelverteilung und fest genug sind, um der Beanspruchung in der Mühle standzuhalten. Dies hat in der Vergangenheit den Zerkleinerungsprozess limitiert. So wurde z.B. eine Zerkleinerungsgrenze um 0.5 μm postuliert [**3, 4**]. Aufgrund dieser Reagglomerationserscheinungen stellt sich nach dem Erreichen einer bestimmten mittleren Partikelgröße ein Gleichgewichtszustand zwischen Agglomeration, Deagglomeration und Bruch ein, so dass trotz steigenden spezifischen Energieeintrags kein weiterer Zerkleinerungsfortschritt beobachtet wird. Dieses Gleichgewicht kann über die interpartikulären Wechselwirkungen und die Mühlenbedingungen eingestellt werden. Mit zunehmender Feinheit der Partikeln werden die interpartikulären Kräfte größer. Die attraktiven Kräfte führen zur Agglomeration, wenn die Partikel kollidieren und wirken somit gegen den Zerkleinerungsprozess. Um diesen Agglomerationsprozess zu verhindern, müssen die Partikeln in der Mühle durch

repulsive Kräfte stabilisiert werden. Dies führt zu kleineren Partikeln. Um ein besseres Verständnis der Vorgänge während des Zerkleinerns unterhalb von 1 μm zu erhalten, muss der Agglomerationsprozeß und dessen Mechanismus genauer untersucht werden. Deswegen wurde in dieser Arbeit ein Schwerpunkt auf den Agglomerationsprozess und die Stabilität gegen Koagulation gesetzt. Es wurden Experimente mit einem gut charakterisierten Modellsystem monodisperser, nanoskaliger Primärpartikeln durchgeführt. Die Suspension wurde unter verschiedenen Bedingungen destabilisiert und agglomeriert. Der Einfluss der Stabilität der Suspension auf den Agglomerationsvorgang wurde unter perikinetischen und orthokinetischen Bedingungen sowie unter Mühlenbedingungen untersucht.

Die gewonnenen Erkenntnisse wurden wegen des großen industriellen Bedarfs an Nanopartikeln in organischen Lösungsmitteln auf nicht wässrige Systeme übertragen. Es konnte gezeigt werden, dass stabile Suspensionen von Al_2O_3 in Ethanol sowohl mit elektrostatischer als auch mit sterischer Stabilisierung erreicht werden können. Zerkleinerungsversuche mit elektrostatischer Stabilisierung zeigen, dass sich der Abrieb negativ auf die Stabilität der Suspension auswirkt. Bei der sterischen Stabilisierung hat der Abrieb keinen Einfluss. Allerdings scheint die Polymerhülle um die Partikeln Teile der Zerkleinerungsenergie zu absorbieren und somit Mahlkörperstöße zu dämpfen. Eine weitere wichtige Frage ist, ob eine mechano-chemische Aktivierung, die während der Zerkleinerung in wässriger Phase beobachtet wurde, eine entscheidende Rolle bei der Nanozerkleinerung spielt.

CHAPTER 2

State of the Art in Wet Media Milling

2.1. Wet Milling in Stirred Media Mills

2.1.1. Influence of Operation Parameters. Stirred media mills belong to the class of comminution machines with loose agitated milling beads. During operation the grinding chamber is filled up to 90% with milling beads. Depending on the milling application the milling beads can consist out of glass, steel, plastics or ceramic. Typically the size of the beads is in the range of 0.1 to 3 mm. In contrast to jar mills, where the motion of grinding beads is generated by rotating the chamber, higher energy inputs can be achieved in stirred media mills, because the energy input in these mills is not restricted by a critical revolution speed. This critical revolution speed in jar mills is reached when the centrifugal force on a milling bead near the wall exceeds the gravitation force. Common rotary speeds in jar mills are in the range of 2/3 to 3/4 of the critical rotary speed. This power limitation results in relative low energy densities. The energy input in stirred media mills is generated in contrast to this by an agitator. Thus higher energy densities can be applied. Stirred media mills are predominantly used for wet milling. They can be operated in continuous or in batch mode. In continuous mode the suspension is pumped axially through the mill. To hold the milling beads back in the mill cutting slits (for milling beads $\geq$ 0.8 mm) or sieving cartridges (for milling beads $\geq$ 0.2 mm) are used. Because smaller milling beads are preferable for the comminution of nanoparticles [**1, 2**], manufacturers of mills offer nowadays centrifugal separation systems. These avoid the plugging of the sieving cartridge or the clamping of milling beads in the cutting slit. In general three types of stirred media mills can be distinguished: stirred media mills with disc stirrers, pinned disk mills or annular gap mills.

Numerical computations showed that around 90% of the energy is dissipated in 10% of the milling chamber volume [**5**]. These regions are close to the stirrer disk tip and the milling chamber wall [**6**]. Hence, grinding media and milling charge have to be transported in these regions. During milling almost 99% of the energy is dissipated into heat [**7, 8, 9**]. This is why the grinding chambers of stirred media mills are in general equipped with double walls for cooling.

An overview on wet grinding technologies for comminution and dispersing of particles is given e.g. by [**9, 10, 11**]. Stirred media mills can be operated in different operation modes. Apart from the batch mode one differentiates the pendulum mode with two receiver vessels and the circuit mode with feedback into a stirred tank. The different operation modes affect thereby the residence

time distribution of the suspension in the mill, which has an effect on the width of the particle size distribution. The narrowest particle size distributions are obtained usually with the pendulum mode.

Fundamental investigations of the operational behavior of stirred media mills and the influences of the different operating parameters (e.g. agitating disk peripheral speed, solid concentration, milling chamber size, flow rate, filling degree of milling media) were accomplished for years at the Institute of Mechanical Process Engineering of the TU Braunschweig. Furthermore, the scale up [**12**], the residence time distribution, the power consumption and the attrition of grinding media was extensively investigated [**13, 14, 15, 16**].

Research of Stehr [**17**] and Weit [**12**] showed that the milling result is dominated by the specific energy (the energy supplied in the milling chamber related to the mass of the product). Further investigations of Bunge [**18**], Thiel [**19**], Joost [**15**], Stadler et al. [**20**] and Mankosa et al. [**21**] showed that apart from the specific energy, the milling media size has an impact on the grinding result. Finer product particles can be achieved with smaller milling beads at the same energy consumption as with larger milling beads. However, a minimum bead size is necessary in order to obtain breakage at all. Kwade [**22**] introduced the characteristic parameters stress energy SE and stress number SN of milling beads. The stress energy is proportional to the maximal kinetic energy of the milling beads:

$$SE \approx \rho_{GM} \cdot v_t^2 \cdot d_{GM}^3. \tag{2.1}$$

This equation can be used for soft and medium hard materials, because in these cases the milling beads are not deformed. By grinding hard materials the deformation of milling beads and the product particles influences the energy transfer during a collision of milling beads. With increasing elastic modulus of the product particles an increasing part of the stress energy is used for the deformation of milling beads. Thus, less energy can be spent for the comminution of product particles. Becker [**16**] approximated the stress energy of the milling beads with a spring model and the Hertz equations as given by Gross et al. [**23**] and expanded the model of Kwade with the Young's modulus of the grinding media E_{GM} and with the Young's modulus of the particles E_p:

$$SE \approx \rho_{GM} \cdot v_t^2 \cdot d_{GM}^3 \cdot \left(\frac{E_{GM}}{E_{GM} + E_p} \right). \tag{2.2}$$

The stress number SN can be approximated according to Kwade [**22**] if the volume concentration of the particles, the filling ratio of milling beads ϕ_{GM}, the porosity of the milling bead bulk freight ϵ_{GM} and the milling time t is known. With the assumption that only one particle is stressed during a collision of milling beads the following equation can be derived:

$$SN \approx \frac{\phi_{GM}\,(1-\epsilon_{GM})}{(1-\phi_{GM}\,(1-\epsilon_{GM}))\,c_v} \cdot n_r \cdot t \cdot \left(\frac{x}{d_{GM}}\right)^2 . \tag{2.3}$$

In figure 2.1 the median particle size is plotted over the stress energy. For each curve in the diagram the specific energy is constant. It is obvious that a certain stress intensity is necessary to achieve breakage at all. With increasing stress energy the median particle size decreases until an optimum is reached. At this optimum a minimal particle size is reached at constant specific energy. With further increasing stress energy the particle size increases. The reason for this is that the stress number decreases with increasing stress energy, if the specific energy is constant. For high stress intensities the stress number is too small to break the particles optimally.

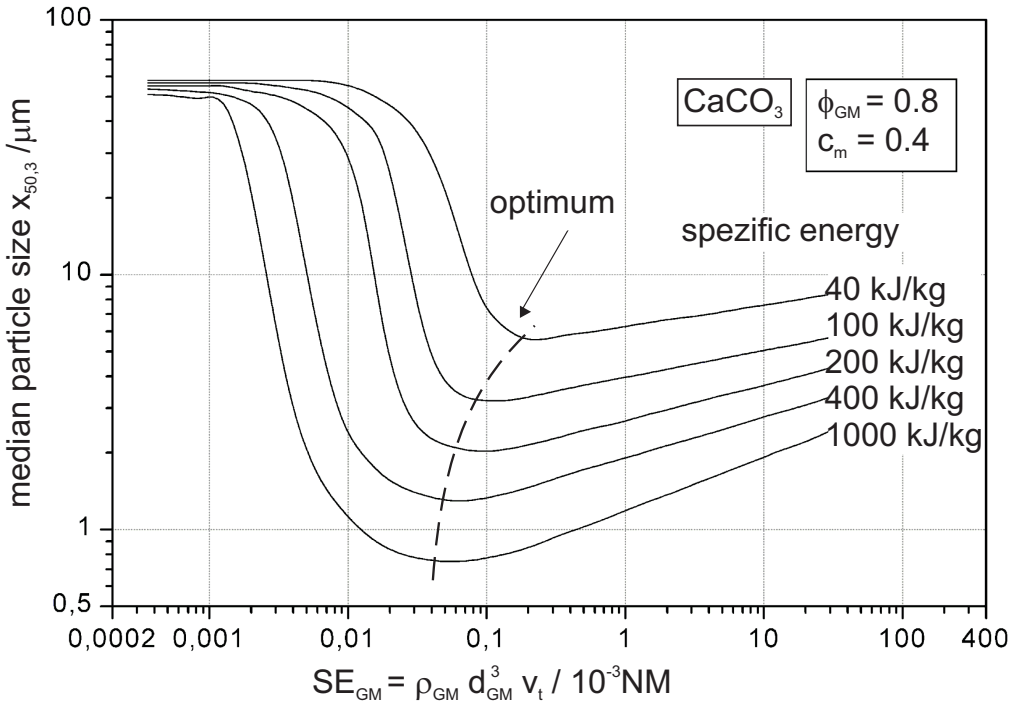

FIGURE 2.1. Optimum of the stress energy of the milling beads for different specific energy inputs for the grinding of limestone [**16**].

Mende [**2**] showed that the concept of stress intensity and stress number can be applied for nano-milling as well. Mende investigated nano-milling of alumina suspensions in aqueous phase. In his experiments the suspensions were stabilized against agglomeration electrostatically. Figure 2.2 shows the median particle size $x_{50,3}$ for α-alumina over the specific energy. For the experiments yttrium stabilized ZrO_2 milling beads with diameters between 200 μm and 1300 μm were used. Furthermore, the suspensions were stabilized at pH5 for the whole milling time. It can be seen, that at constant specific energy inputs smaller product particle sizes can be reached with decreasing milling bead

diameter. Furthermore, in these experiments product particles below 10 nm could be produced without reaching a grinding limit.

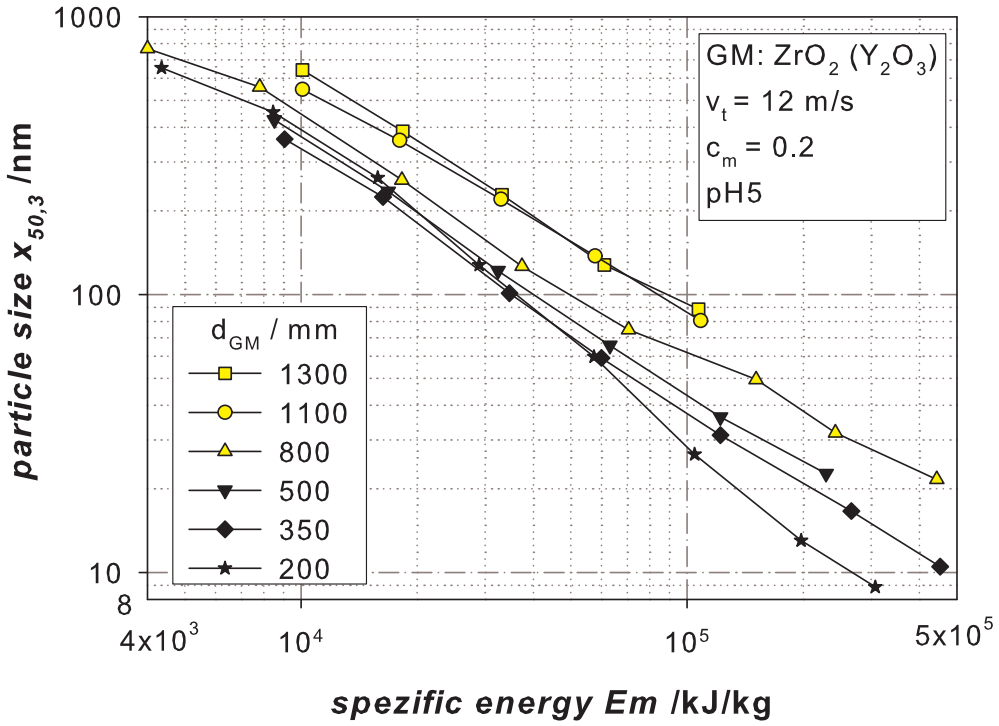

FIGURE 2.2. Influence of the milling bead diameter on the milling of alumina with yttrium stabilized milling beads [**14**].

Stenger [**1**] investigated the influence of inter-particle interactions on nano-milling in stirred media mills in aqueous phase and electrostatic stabilization and found that the grinding progress is determined mainly by the superposition of breakage, agglomeration and deagglomeration. The final particle size depends on the stability conditions of the suspension. At good stability conditions final particle sizes measured with an ultrasonic spectrometer of $x_{50,3} \leq 50$ nm for Al_2O_3 and $x_{50,3} \leq 20$ nm for SnO_2 could be achieved. On the other hand the smallest final particle sizes for the material SiO_2 and TiO_2 are only in the size range between 160 and 180 nm. The milling conditions were carefully optimized for alumina and tin oxide, but not yet for titania and silica, so that even finer sizes may be possible for the latter materials.

Stenger further showed that milling of alumina particles in water is strongly influenced by mechano-chemical changes. During milling alumina hydroxide is formed, which dissolves and influences in that way the grinding behavior in the sub micron size range. This fact might explain the possibility to "grind" alumina particles down to median particles sizes below 10 nm. However, by milling SnO_2 no influence of mechano-chemistry was detected at all. Crystallite sizes obtained von Rietveld analysis of the XRD spectrum (line broadening) was almost similar to BET based diameters, i.e. almost single crystals were obtained